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(56) Documents cited

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(58) Field of search

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(71) Applicant

Kao Soap Co. Ltd.,

14—10 Nihonbashi-

Kayabacho,

1-chome,

Chuo-ku,

Tokyo,

Japan

(72) Inventors

Moriyasu Murata

Kouki Horikoshi

Akira Suzuki

(74) Agents

Withers and Rogers,

4, Dyer's Buildings,

Holborn,

London,

EC1N 2JT

(54) Enzyme detergent composition

(57) A detergent composition
comprising an alkali cellulase is
particularly effective for removing

solid, inorganic dirt and enhances the
deterging effect of phosphorus free or
low phosphorus content detergents.
The cellulase may be obtained from
Bacillus or *Aeromonas* species.

GB 2 095 275 A

SPECIFICATION

Detergent composition

The present invention relates to a detergent composition. More particularly, the present invention relates to a detergent composition characterised by containing an alkali cellulase which exhibits high activity under alkaline conditions. 5

Recently, techniques of cleansing clothes have been remarkably developed. The washing of clothes has been facilitated greatly by the development of detergent materials, water conditioning, improvements in and increases in the spread of washing machines and improvements in fibers. Among them, the improvement of the starting materials for detergents is remarkable. Owing to the 10 improvements in surfactants, builders, dispersants, fluorescent dyes and bleaching agents, the compositions of detergents for clothes have nearly reached the stage of completion. Detergents for clothes are based on the following principles: 10

(1) A surfactant or builder is adsorbed on the dirt or/and fiber surface to reduce the surface tension between the dirt or/and fiber and water, so that the dirt is physico-chemically separated out of the fiber. 15

(2) The dirt is dispersed and solubilized by means of a surfactant or inorganic builder.

(3) The dirt is chemically decomposed by an enzyme such as protease.

(4) Coloured stains are bleached with a bleaching agent.

(5) A fluorescent dye is adsorbed on the fiber surface to brighten it.

(6) The precipitation of active detergent ingredients by divalent metal ions is prevented by means of a chelating agent. 20

The fundamental idea of cleansing clothes in the prior art is the incorporation of a component which directly attacks the dirt or a component which enhances the attacking power of said active ingredient in the composition. At present, the effectiveness of the known detergent compositions based on this fundamental idea have almost reached an optimum level and great efforts will be required if 25 further improvement are to be made. 25

After intensive investigations from viewpoints different from the conventional ideas of the deterging of clothes, the inventors have found that, unexpectedly, quite excellent deterging effects on types of dirt which are generally not concerned with enzymatic activity of an alkali cellulase (one of the cellulase enzymes) are obtained if the alkali cellulase is incorporated in a detergent. The present 30 invention has been completed on the basis of this finding. 30

Commercially available or generally well-known cellulases have an optimum pH under acidic or neutral conditions and their use under alkaline conditions has generally been avoided, since their activity has been reduced under such conditions.

The present invention provides a detergent composition characterised by containing an alkali cellulase having an alkaline pH as its optimum pH. According to the present invention, there is provided a detergent composition having a remarkable deterging effect particularly on inorganic types of dirt which are generally not concerned with alkali cellulase activity at all. 35

As described above, it has been known in the art to use an enzyme as a component of a detergent. As such enzymes, there have been used only those which effectively act on the dirt. More particularly, there have been used only protease for protein stains, amylase for saccharide stains and lipase for oily and fatty stains. Those enzymes attack the stains directly. Though the mechanism of the deterging effects of the alkali cellulase in the present invention have not fully been elucidated, it is known that the effects are not merely based on an expansion of the fibers, unlike phenomena observed 45 when surfactants are used. 45

The main advantages of the present invention are that the detergent is particularly effective for removing solid inorganic dirt such as fine mud particles which cannot be removed sufficiently with conventional detergents and also for removing other types of dirt such as the stains on the necks and cuffs of clothes and oily stains on clothes and that it is highly useful for enhancing the deterging power of phosphorus-free detergents and detergents having only a low phosphorus content. Phosphate salts 50 have been effective for the removal of fine mud particles that has penetrated into the fibers. However, there is nowadays a desire to reduce the amount of phosphate salts incorporated into detergents because of the problem of eutrophication. The requirement for the use of phosphate-free detergents makes the removal of mud particles extremely difficult. In particular, the removal of mud particles from cotton clothing is quite difficult, as is well known. Further, muddy stains on canvas shoes have proved 55 difficult to remove. 55

The present invention throws a fresh light on the above-mentioned problems. According to the present invention, an excellent deterging power equivalent or superior to that of a weak alkaline powdery detergent containing sufficient phosphate salt can be obtained by, for example, (1) applying 60 the present invention to an alkaline detergent containing no phosphates or a small amount of phosphates or (2) applying the present invention to a weakly alkaline, liquid, phosphate-free detergent in the cleaning of muddy stains in cellulose fibers or blended fiber cloths comprising cellulose fibers and other fibers. 60

Another great advantage of the present invention is that it can be applied to detergents of any

shape. The alkali cellulase may be incorporated in a composition in the form of any of spray-dried powder, powder-blended powder, tablets or liquid to obtain the detergent composition of the present invention.

The alkali cellulases used in the present invention are those having an optimum pH of 8.0—11.5, preferably 8.1—11.0. Under alkaline conditions, those enzymes exhibit an activity equivalent to that exhibited under acidic or neutral conditions. The alkali cellulases are obtained from cellulase culture liquids of various origins by refining and fractionation according to salting out, precipitation, dialysis or gel permeation method. The alkali cellulases are obtained also by fractionation of crude enzymes or refined enzymes according to electrophoresis or by the heat treatment of the same (for example, at 40—90°C for 0.5 min to 3h).

As particularly preferred alkali cellulases used in the present invention, the following enzymes may be mentioned:

The specific cellulase to be used in the invention is preferably a cellulase produced by a fungus of *Bacillus N* or a cellulase 212-producing fungus belonging to the genus *Aeromonas*. The *Bacillus N* is disclosed in Japanese patent publication No. 28515/75 and available from the Fermentation Research Institute, the Agency of Industrial Science and Technology, located at 1-1-3, Higashi, Tsukuba-Yatabe-machi, Ibaraki, Japan. It has been added to its permanent collection of micro-organisms as deposition numbers, FERM Nos. 1138, 1139, 1140 and 1141. The *Aeromonas* fungus has been added also to the permanent collection of microorganism in the Fermentation Research Institute, the Agency of Industrial Science and Technology, as FERM No. 2306 and is disclosed in Japanese patent publication (unexamined) No. 76287/75, now published after examination as Japanese patent publication No. 39191/81.

The cellulase to be used in the invention includes a cellulase extracted from the hepatopancreas of a marine mollusc (*Dolabella Auricula Solander*), which is disclosed in *Biochem. J.* (1966) 99, 214—221.

Each of celluloses produced by these fungi is a special cellulase which retains a high activity even under alkaline conditions and has an alkali resistance.

The detergent composition of the present invention is characterized in that this special cellulase is contained as one indispensable ingredient. More particularly, the present invention provides a detergent composition having a prominent washing power to inorganic stains irrelevant to the inherent activity of the cellulase, especially collar contaminations consisting of mixtures of inorganic stains and oils secreted on the skin surface, which change with the lapse of time.

When the detergent composition comprising a special cellulase having a high activity under alkaline conditions and also having an alkali resistance, which is produced by a fungus selected from *Bacillus N* (deposited with FRI deposition numbers of 1138 through 1141) and a cellulase 212-producing fungus belonging to the genus *Aeromonas*, is employed, an excellent washing effect can be obtained over a broad range of the pH value of the washing bath.

This excellent effect overbalances reduction of the washing power due to reduction of the alkali capacity of the builder on reduction of the pH value of the washing bath.

The enzymatic activity of the cellulase that is used in the present invention is determined according to the following method.

50mg of Avicel (for chromatography) or carboxymethyl cellulose (CMC) is suspended in 4ml of a glycine NaCl-NaOH buffer solution (having a pH value of 8.3), and the suspension is preheated at 37°C for 5 minutes and 1ml of an enzyme liquid is added to the suspension. The suspension is sufficiently mixed and reaction is carried out for 1 hour. After completion of the reaction, the quantity of reduced sugar is determined according to the 3,5-dinitrosalicylic acid method. More specifically, the liquid reaction mixture is filtered, and 3ml of 3,5-dinitrosalicylic acid is added to 1 ml of the filtrate and the mixture is heated at 100°C for 10 minutes to effect coloration. The mixture is cooled and is then mixed with deionized water so that the total volume is increased to 25ml. The resulting liquid is subjected to colorimetry at a wavelength of 500mμ.

When 1mg of the enzyme as the solid produces reduced sugar in an amount corresponding to 1μ mole of glucose for 1 hour under the above conditions, the enzymatic activity is defined as 1 unit per mg of the solid.

The present invention is attained by combining those alkali cellulases with well-known detergent compositions. As for the alkali cellulase content, it is preferred that the composition contains 0.01—70 wt.%, particularly 0.1—10 wt.%, of an alkali cellulase having an enzymatic activity of at least 0.001 unit/mg solid [1 unit/mg solid forms 10μ mol of glucos from cellulose in one hour at 37°C at pH 8.3]. Also the amount of the alkali cellulase is such that enzymatic activity of alkali cellulase in the bath is preferably 0.1—1000 units/l, more particularly, 1—100 units/l.

Though the detergent composition of the present invention can be used in an unlimited pH range of from acidic to alkaline pH, it is preferred in order to sufficiently exhibit the detergent effect of the alkali cellulase that the detergenting bath is alkaline (more particularly, it has pH 7—11).

In the detergent composition of the present invention, components other than cellulase are not particularly limited. For example, the following components may be incorporated in the composition according to their essential properties:

[1] **Surfactants:**

(1) Straight-chain or branched alkylbenzenesulfonate salts having an alkyl group of 10—16 carbon atoms in average.

(2) Alkyl or alkenyl ether sulfate salts having a straight-chain or branched alkyl or alkenyl group of 10—20 carbon atoms in average, 0.5—8 mol in average of ethylene oxide, propylene oxide or butylene oxide in the molecule and an addition ratio of ethylene oxide/propylene oxide of 0.1/9.9—9.9/0.1 or ethylene oxide/butylene oxide of 0.1/9.9—9.9/0.1.

(3) Alkyl or alkenyl sulfate salts having an alkyl or alkenyl group of 10—20 carbon atoms in average.

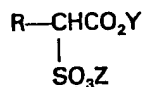
(4) Olefinsulfonate salts having 10—20 carbon atoms in average in the molecule.

(5) Alkanesulfonate salts having 10—20 carbon atoms in average in the molecule.

(6) Saturated or unsaturated fatty acid salts having 10—24 carbon atoms in average in the molecule.

(7) Alkyl or alkenyl ether carboxylate salts having an alkyl or alkenyl group of 10—20 carbon atoms in average, 0.5—8 mol in average of ethylene oxide, propylene oxide or butylene oxide in the molecule and an addition ratio of ethylene oxide/propylene oxide of 0.1/9.9—9.9/0.1 or ethylene oxide/butylene oxide of 0.1/9.9 to 9.9/0.1.

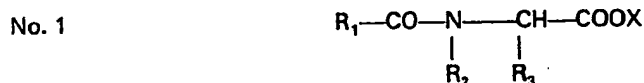
(8) α -Sulfo fatty acid salts or esters of the general formula:



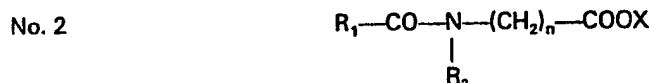
wherein Y represents an alkyl group having 1—3 carbon atoms or a counter-ion, Z represents a counter-ion and R represents an alkyl or alkenyl group having 10—20 carbon atoms.

As the counter-ions of anionic surfactants, there may be mentioned, for example, ions of alkali metals such as sodium and potassium, alkaline earth metals such as calcium and magnesium, ammonium, alkanolamines containing 1—3 alkanol groups having 2 or 3 carbon atoms such as monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine.

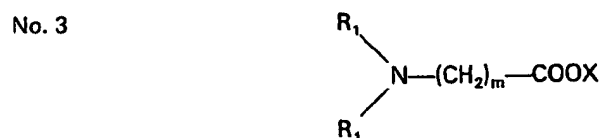
(9) Amino acid-type surfactants of the general formulae:



wherein R_1 represents an alkyl or alkenyl group having 8—24 carbon atoms, R_2 represents hydrogen or an alkyl group having 1—2 carbon atoms, R_3 represents an amino acid residue and X represents an alkali metal or alkaline earth metal ion.



wherein R_1 , R_2 and X have the same meanings as above and n represents an integer of 1—5.



wherein R_1 has the same meaning as above and m represents an integer of 1—8.

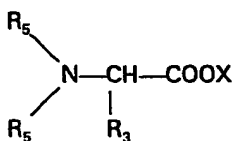


wherein R_1 , R_3 and X have the same meaning as above and R_4 represents hydrogen, or an alkyl or hydroxyalkyl group having 1—2 carbon atoms.



wherein R_2 , R_3 and X have the same meaning as above and R_5 represents a β -hydroxyalkyl or β -hydroxyalkenyl group having 6—28 carbon atoms.

No. 6

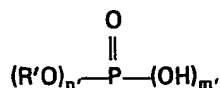


wherein R_3 , R_5 and X have the same meaning as above.

(10) Phosphate ester surfactants:

No. 1 Acid alkyl (or alkenyl) phosphates:

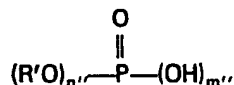
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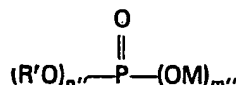
wherein R' represents an alkyl or alkenyl group having 8—24 carbon atoms, $n' + m'$ represents 3 and n' represents a number of 1—2.

No. 2 Alkyl (or alkenyl) phosphates:



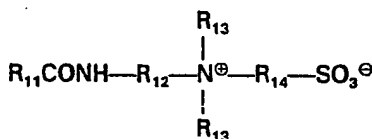
10 wherein R' has the same meaning as above, $n'' + m''$ represents a number of 3 and n'' represents a number of 1—3. 10

No. 3 Alkyl (or alkenyl) phosphate salts:



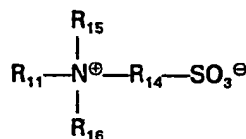
15 wherein R' , n'' and m'' have the same meaning as above and M represents Na, K or Ca. 15

No. 1



wherein R_{11} represents an alkyl or alkenyl group having 8—24 carbon atoms, R_{12} represents an alkylene group having 1—4 carbon atoms, R_{13} represents an alkyl group having 1—5 carbon atoms, R_{14} represents an alkylene or hydroxyalkylene group having 1—4 carbon atoms.

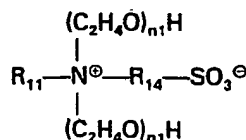
20 No. 2



20

wherein R_{11} and R_{14} have the same meaning as above and R_{15} and R_{16} each represent an alkyl or alkenyl group having 8—24 or 1—5 carbon atoms.

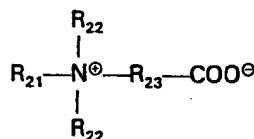
No. 3



25 wherein R_{11} and R_{14} have the same meaning as above and n_1 represents an integer of 1—20. 25

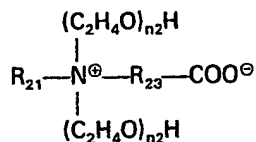
(12) Betaine-type, amphoteric surfactants of the general formulae:

No. 1



wherein R_{21} represents an alkyl, alkenyl, β -hydroxyalkyl or β -hydroxyalkenyl group having 8—24 carbon atoms, R_{22} represents an alkyl group having 1—4 carbon atoms and R_{23} represents an alkylene or hydroxyalkylene group having 1—6 carbon atoms.

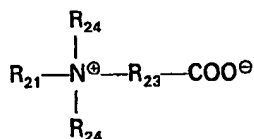
No. 2



5 wherein R_{21} and R_{23} have the same meaning as above and $n2$ represents an integer of 1—20.

5

No. 3



wherein R_{21} and R_{23} have the same meaning as above and R_{24} represents a carboxyalkyl or hydroxyalkyl group having 2—5 carbon atoms.

10 (13) Polyoxyethylene alkyl or alkenyl ethers having an alkyl or alkenyl group of 10—20 carbon atoms in average and 1—20 mol of ethylene oxide added.

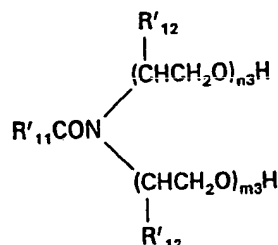
(14) Polyoxyethylene alkylphenyl ethers having an alkyl group of 6—12 carbon atoms in average and 1—20 mol of ethylene oxide added.

(15) Polyoxypropylene alkyl or alkenyl ethers having an alkyl or alkenyl group of 10—20 carbon atoms in average and 1—20 mol of propylene oxide added.

15 (16) Polyoxybutylene alkyl or alkenyl ethers having an alkyl or alkenyl group of 10—20 carbon atoms in average and 1—20 mol of butylene oxide added.

(17) Nonionic surfactants having an alkyl or alkenyl group of 10—20 carbon atoms in average and 1—30 mol in total of ethylene oxide and propylene oxide added or ethylene oxide and butylene oxide added (ratio of ethylene oxide to propylene oxide or butylene oxide being 0.1/9.9 to 9.9/0.1).

20 (18) Higher fatty acid alkanolamides or alkylene oxide adducts thereof of the general formula:

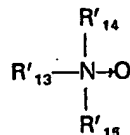


wherein R'_{11} represents an alkyl or alkenyl group having 10—20 carbon atoms, R'_{12} represents H or CH_3 , $n3$ represents an integer of 1—3 and $m3$ represents an integer of 0—3.

25 (19) Sucrose/fatty acid esters comprising fatty acids having 10—20 carbon atoms in average and sucrose.

(20) Fatty acid/glycerol monoesters comprising fatty acids having 10—20 carbon atoms in average and glycerol.

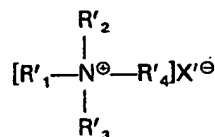
(21) Alkylamine oxides of the general formula:



30 wherein R'_{13} represents an alkyl or alkenyl group having 10—20 carbon atoms and R'_{14} and R'_{15} each represent an alkyl group having 1—3 carbon atoms.

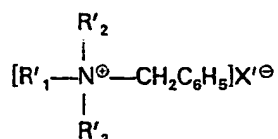
(22) Cationic surfactants of the general formulae:

No. 1



wherein at least one of R'_1 , R'_2 , R'_3 and R'_4 represents an alkyl or alkenyl group having 8—24 carbon atoms and the remainder represents an alkyl group having 1—5 carbon atoms and X' represents a halogen.

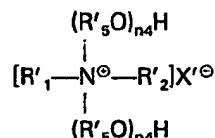
No. 2



5 wherein R'_1 , R'_2 , R'_3 and X' have the same meaning as above.

5

No. 3



wherein R'_1 , R'_2 and X' have the same meaning as above, R'_5 represents an alkylene group having 2—3 carbon atoms and $n4$ represents an integer of 1—20.

The composition preferably contains at least one of the above surfactants in an amount of at least 10 wt.%. 10

As preferred surfactants, there may be mentioned above surfactants 1), 2), 3), 4), 5), 6), 11)-No. 2, 12)-No. 1, 13), 14), 15), 17) and 18).

[2] Divalent metal ion sequestering agents:

The composition may contain 0—50 wt.% of one or more builder components selected from the 15 group consisting of alkali metal salts or alkanolamine salts of the following compounds:

1) Salts of phosphoric acids such as orthophosphoric acid, pyrophosphoric acid, tripolyphosphoric acid, metaphosphoric acid, hexametaphosphoric acid and phytic acid. 15

2) Salts of phosphonic acids such as ethane-1,1-disphosphonic acid, ethane,1,1,2-triphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid and its derivatives, ethane-hydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid and methanediolhydroxyphosphonic acid. 20

3) Salts of phosphono carboxylic acids such as 2-phosphonobutane-1,2-dicarboxylic acids, 1-phosphonobutane-2,3,4-tricarboxylic acids and α -methylphosphonosuccinic acid.

4) Salts of amino acids such as aspartic acid, glutamic acid and glycine.

5) Salts of aminopolyacetic acids such as nitrilotriacetic acid, iminodiacetic acid, ethylenediaminetetracetic acid, diethylenetriaminepentaacetic acid, glycol ether diaminetetraacetic acid, hydroxyethyliminodiacetic acid, triethylenetetraminehexaacetic acid and dienkollic acid. 25

6) High-molecular electrolytes such as polyacrylic acid, polyaconitic acid, polyitaconic acid, polycitractonic acid, polyfumaric acid, polymaleic acid, polymesaconic acid, poly- α -hydroxyacrylic acid, polyvinylphosphonic acid sulphonated polymaleic acid, maleic anhydride/diisobutylene copolymer, maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic anhydride/ethylene 30 copolymer, maleic anhydride/ethylene cross-linked copolymer, maleic anhydride/vinyl acetate copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylate ester copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoprene copolymer, poly- β -keto carboxylic acid derived from maleic anhydride and carbon monoxide, itaconic acid/ethylene copolymer, itaconic acid/aconitic acid copolymer, itaconic acid/maleic acid copolymer, Itaconic acid/acrylic acid copolymer, 35 malonic acid/methylene copolymer, mesaconic acid/fumaric acid copolymer, ethylene glycol/ethylene terephthalate copolymer, vinylpyrrolidone/vinyl acetate copolymer, 1-butene-2,3,4-tricarboxylic acid/itaconic acid/acrylic acid copolymer, quaternary ammonium group-containing polyester polyaldehyde carboxylic acids, cis-isomer of epoxysuccinic acid, poly[N,N-bis(carboxymethyl)acrylamide], poly(hydroxy carboxylic acid), starch succinate, starch maleate, starch 40 terephthalate, starch phosphate ester, dicarboxystarch, dicarboxymethylstarch and cellulose succinate esters.

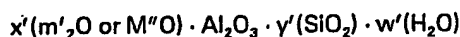
7) Non-dissociating high-molecular compounds such as polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and cold water-soluble, urethanated polyvinyl alcohol. 45

8) Salts of dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and decan-1,10-dicarboxylic acid; salts of diglycolic acid, thiodiglycolic acid, oxalacetic acid, hydroxydisuccinic acid, carboxymethylhydroxysuccinic acid and carboxymethyltartronic acid; salts of hydroxy carboxylic acids such as glycolic acid, malic acid, hydroxypivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and 50 dialdehyde starch oxide; salts of itaconic acid, methylsuccinic acid 3-methylglutaric acid, 2,2-dimethylmalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butene-1,2,3-tricarboxylic acid, butane,1,2,3,4-tetracarboxylic acid,

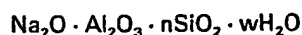
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ethanetetra-carboxylic acid, ethenetetracarboxylic acid, n-alkenylaconitic acid, 1,2,3,4-cyclopentanetetra-carboxylic acid, phthalic acid, trimesic acid, hemimellitic acid, pyromellitic acid, benzenehexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-tetracarboxylic acid; salts of sulfonated carboxylic acids such as sulfoitaconic acid, sulfotricarballylic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylated sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylated gluconic acid, condensates of polyhydric alcohols or saccharides with maleic anhydride or succinic anhydride, condensates of hydroxy carboxylic acids with maleic anhydride or succinic anhydride, and organic acid salts such as CMOS and Builder M.

10 9) Aluminosilicates: 10
No. 1 Crystalline aluminosilicates of the formula:



wherein M' represents an alkali metal atom, M'' represents an alkaline earth metal atom exchangeable with calcium, and x', γ' and w' represent mole numbers of the respective components and generally, 15 they are as follows: $0.7 \leq x' \leq 1.5$, $0.8 \leq \gamma' \leq 6$ and w' being a positive number. 15
No. 2 Detergent builders having the following general formula are particularly preferred:



wherein n represents a number of 1.8—3.0 and w represents a number of 1—6.
No. 3 Amorphous aluminosilicates of the formula:

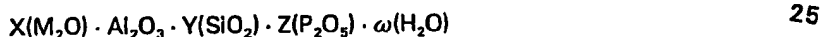
20 $x(M_2O) \cdot Al_2O_3 \cdot \gamma(SiO_2) \cdot w(H_2O)$ 20

wherein M represents sodium and/or potassium atom, and x, γ and w represent mole numbers of the respective components within the following ranges:

$$0.7 \leq x \leq 1.2$$

$$1.6 \leq \gamma \leq 2.8$$

25 w: any positive number including 0.
No. 4 Amorphous aluminosilicates of the formula:



wherein M represents Na or K and X, Y, Z and ω represent mole numbers of the respective components within the following ranges:

30 $0.20 \leq X \leq 1.10$ 30

$$0.20 \leq Y \leq 4.00$$

$$0.001 \leq Z \leq 0.80$$

ω : any positive number including 0.

[3] Alkalis or inorganic electrolytes:
35 The composition may contain also 1—50 wt.%, preferably 5—30 wt.%, of one or more alkali metal salts selected from the following compounds as the alkali or inorganic electrolyte: silicates, carbonates and sulfates. Further, the composition may contain organic alkalis such as triethanolamine, diethanolamine, monoethanolamine and triisopropanolamine. 35

[4] Antiredeposition agents:
40 The composition may contain 0.1—5% of one or more of the following compounds as antiredeposition agent(s): polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and carboxymethylcellulose. 40

Particularly, a combination of carboxymethylcellulose or polyethylene glycol with the alkali cellulase of the present invention exhibits a synergism in the removal of muddy dirt.
45 In order to avoid the decomposition of carboxymethylcellulose by the alkali cellulase in the detergent composition, it is preferred that the carboxymethylcellulose is used in a granular or coated form. 45

[5] Bleaching agents:

A combination of the alkali cellulase of the present invention with a bleaching agent such as sodium percarbonate, sodium perborate, sodium sulfate/hydrogen peroxide adduct or sodium chloride/hydrogen peroxide adduct or/and a photosensitive bleaching dye such as zinc or aluminum salt of sulfonated phthalocyanine further improves the deterging effects.

[6] Enzymes (enzymes which exhibits the essential enzymatic effects thereof in the deterging step):
As the enzymes, the following enzymes may be mentioned (classified with respect to their enzymatic reactivities):

Hydrolases, hydrases, oxido-reductases, desmolases, transferases and isomerases. All of these enzymes may be used in the present invention. Particularly preferred enzymes are hydrolases such as proteases, esterases, carbohydrolases and nucleases.

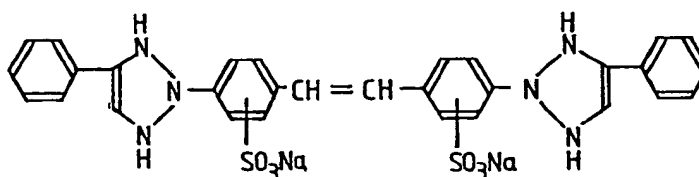
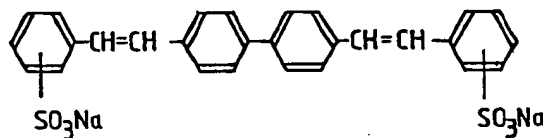
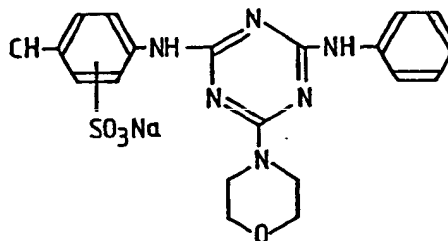
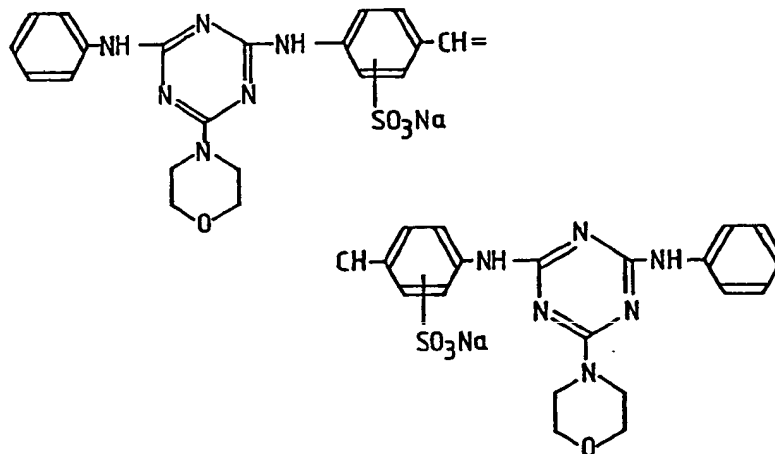
Examples of proteases are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN, papain, bromelin, carboxypeptidases A and B, aminopeptidase and aspergillopeptidases A and B.

Examples of esterases are gastric lipase, pancreatic lipase, vegetable lipases, phospholipases, cholinesterases and phosphotases.

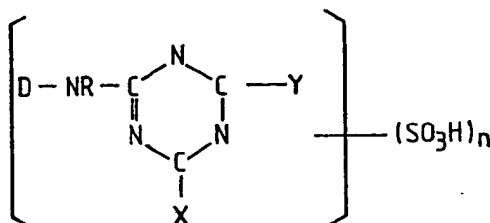
Carbohydrolases other than alkali cellulases include maltase, saccharase, amylase, pectinase, lysozyme, α -glucosidase and β -glucosidase.

[7] Bluing agents and fluoroescnet dyes:

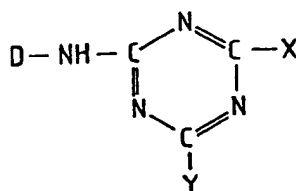
Various bluing agents and fluoroescnet dyes may be incorporated in the composition, if necessary. For example, compounds of the following structures are recommended:



and bluing agents of the general formulae:



wherein D represents a residue of blue or purple, monoazo, disazo or anthraquinone dye, X and Y each represent hydroxyl group, amino group, an aliphatic amino group which may be substituted with hydroxyl, sulfonic acid, carboxylic acid or alkoxyl group, or an aromatic or alicyclic amino group which may be substituted with a halogen atom or hydroxyl, sulfonic acid, carboxylic acid, lower alkyl or lower alkoxyl group, R represents a hydrogen atom or a lower alkyl group but excluding cases wherein (1) R represents a hydrogen atom and both X and Y represent a hydroxyl group or an alkanolamine at the same time and (2) R represents a hydrogen atom, one of X and Y represents a hydroxyl group and the other represents an alkanolamine group, and n represents an integer of at least 2, and



wherein D represents a residue of a blue or purple, azo or anthraquinone dye, and X and Y may be the same or different and represent an alkanolamine residue or a hydroxyl group.

[8] Caking-preventing agents:

The following caking-preventing agents may be incorporated in powdery detergent composition: p-toluenesulfonate salts, xylenesulfonate salts, acetate salts, sulfosuccinate salts, talc, finely pulverized silica, clay, calcium silicates (such as Micro-cell of Johns-Manvill Co.), calcium carbonate and magnesium oxide.

[9] Masking agents for factors inhibiting the alkali cellulase activity:

The alkali cellulases are deactivated in some cases in the presence of copper, zinc, chromium, mercury, lead, manganese or silver ions or their compounds. Various metal chelating agents and metal-precipitating agents are effective on these inhibitors. They include, for example, divalent metal ion sequestering agents as listed in the above item [2] with reference to optional additives as well as magnesium silicate and magnesium sulfate.

Cellobiose, glucose and gluconolactone act sometimes as the inhibitors. It is preferred to avoid the co-presence of those saccharides with the alkali cellulase as far as possible. In case the co-presence is unavoidable, it is necessary to avoid the direct contact of the saccharides with the alkali cellulase by, for example, coating them.

Strong chelating agents such as ethylenediaminetetraacetate salts, anionic surfactants and cationic surfactants act as the inhibitors in some cases. However, the co-presence of those substances with the alkali cellulase is allowable if the direct contact of them is prevented by some ideas such as tableting and coating methods.

The above-mentioned masking agents and methods may be employed, if necessary, in the present invention.

[10] Alkali cellulase-activators:

The activators vary depending on variety of the alkali cellulases. In the presence of proteins, cobalt and its salts, calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose, the alkali cellulases are activated and their deterging powers are improved remarkably.

[11] Anti oxidants:

The antioxidants include, for example, tert-butylhydroxytoluen, 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-butylidenebis(6-tert-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phenol, distyrenated phenol and 1,1'-bis(4-hydroxyphenyl)cyclohexane.

[12] Solubilizers:

The solubilizers include, for example, low molecular alcohols such as ethanol, benzenesulfonate salts, lower alkylbenzenesulfonate salts such as p-toluenesulfonate salts, glycols such as propylene glycol, acetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea.

- 5 The following examples will further illustrate the present invention. In the following referential example, the preparation of an alkali cellulase is explained. Unless otherwise stated, percentages in the following examples are given by weight. 5

Referential Example 1**Preparation of alkali cellulase:**

- 10 Alkali-resistant cellulases according to the present invention are obtained by, for example, a technique disclosed in G. Okada, T. Nishizawa and K. Nishizawa "Biochem. J., 99, 214 (1966)". More particularly, a crude enzyme solution was extracted from the hepatopancreas of a marine mollusc (Dolabella sp.). The crude enzyme solution was subjected to the starch zone-electrophoresis and carboxymethylcellulose-saccharifying activity of the resulting fraction was measured. The 10
- 15 carboxymethylcellulose-saccharifying activity of pH 8.3 was determined from an absorbance (ΔOD) at 660 m μ using an alkaline copper reagent and arsenomolybdate after reacting the fraction with carboxymethylcellulose. 15

	Fraction No.	Cellulase Activity at pH 8.3 (ΔOD)	
20	10	0.05	20
	15	0.55	
	20	0.47	
	30	0.40	
	35	0.12	

- 25 It is understood that fractions Nos. 15, 20 and 30 contain cellulases having a high activity under a weak alkaline condition. 25

Example 1

Effects of alkali cellulase superior to those of other enzymes on cotton cloths artificially stained with muddy dirt will be shown:

30 1) Detergent compositions:

		A (%)	B (%)	
	Sodium straight-chain dodecylbenzenesulfonate	10	—	
35	Sodium α -olefinsulfonates (C ₁₆₋₁₈)	5	—	35
	Sodium alkylethoxysulfates (C ₁₄₋₁₅ , EO=1.5 mols)	2	25	
	Sodium alkyl sulfates (C ₁₄₋₁₅)	3	—	
40	Soap (beef fatty acid sodium salts)	2	—	
	Secondary alcohol (C=13.5) ethoxylate (EO=7)	—	25	40
	Sodium tripolyphosphate	10	—	
	Crystalline sodium aluminosilicate (type 4A)	10	—	
45	Sodium silicate	10	—	45
	Triethanolamine	—	5	
	Sodium carbonate	10	—	
	Potassium carbonate	—	5	
	Carboxymethylcellulose	1	1	
50	Polyethylene glycol (MW 6000)	1	1	50
	Fluorescent dye	0.4	0.3	
	Blueing agent	—	0.05	
	Sodium p-toluenesulfonate	2	—	
	Ethanol	—	8	
55	Water	10	balance	55
	Enzyme	0 or 3	0 or 2	
	Perfume	0.2	0.1	
	Glauber's salt	balance	—	

2) Mud-stained cloths (artificially stained cloths):

Kanuma sekigyoku soil for horticultural use was dried at $120^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 4 h and then pulverized. 150 mesh (100 μm)-passed soil particles were dried at $120^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 2 h. 150 g of the soil particles was dispersed in 1000 l of Perclene. A calico #2023 cloth was contacted with the dispersion and brushed. After removal of the dispersion, excessive mud remaining on the cloth was removed (Japanese Patent Laid-Open No. 26473/1980).

Test pieces having a size of 10 cm x 10 cm were prepared and subjected to the tests.

3) Deterging conditions and method and appraisal:

A detergent was dissolved in 4°DH hard water to obtain 1 l of 0.133% aqueous detergent solution. Five pieces of the cloth artificially stained with the muddy dirt were immersed in the aqueous detergent solution. After leaving them to stand at 40°C for 2 hours, the detergent solution and the pieces of artificially stained cloth were transferred in a stainless steel beaker for Turgotometer and stirred at 100 rpm at 20°C for 10 minutes in the Turgotometer. After washing with running water, they were pressed with an iron and their reflectivities were measured. The deterging rate was calculated according to the following formula:

Reflectivities of the original cloth before the washing and those of the stained cloth before and after the washing were measured by means of an automatic recording colorimeter (a product of Shimadzu Seisaku-sho) and the deterging rate (%) was calculated according to the following formula:

$$\text{Deterging rate (\%)} = \frac{\frac{(\text{Reflectivity after washing}) - (\text{Reflectivity before washing})}{(\text{Reflectivity of original cloth}) - (\text{Reflectivity before washing})} \times 100}{1}$$

An average of fives samples was shown in Table 1. The aqueous detergent solution before the washing had pH 10.6.

4) Enzymes used:

- (1) Not used (balanced with Glauber's salt) (comparative)
- (2) Alkali cellulase (crude enzyme solution of fraction No. 15 in the above referential example)
- (3) Alkali cellulase (crude enzyme solution of fraction No. 20 in the above referential example)
- (4) Alkali cellulase (crude enzyme solution of fraction No. 30 in the above referential example)
- (5) Cellulase (crude enzyme solution of fraction No. 35 in the above referential example)
- (6) Amylase (Termamyl 60 G; a product of Novo Co.)
- (7) Protease (Gist Brocades, maxatase P 330,000)
- (8) Lipase (Olipase; a product of Nagase Sangyo Co.)

5) Results:

Table 1

	Enzyme in the Detergent	Deterging rate (%)	
		Composition A	Composition B
45	①	65	60
	②	81	78
	③	80	77
	④	79	76
	⑤	74	72
50	⑥	66	—
	⑦	65	—
	⑧	65	—

Referential Example 2

- 5 A culture medium (having a pH value of 10) containing 1.0% of peptone, 1.0% of meat extract, 1.0% of carboxymethyl cellulose (CMC), 0.5% of sodium chloride, 0.1% of potassium dihydrogen phosphate and 1.0% of anhydrous sodium carbonate was inoculated with *Bacillus* N4, a novel species belonging to the genus *Bacillus* (deposited with the FRI deposition number of 1141), separated from the soil collected at Hirosawa, Wako city, Saitama prefecture, and shaking culturing was carried out 37°C for 72 hours. Cells were removed by centrifugal separation to obtain a crude enzyme. The crude enzyme was dried with ethanol according to the customary method to obtain a cellulase powder. Thus, 10 g/l of a cellulase enzyme (having an enzymatic activity of 0.6 unit/mg of the solid at a pH value of 6) (hereinafter referred to as "cellulase N-4") was obtained.
- 10 At a pH value of 9, the so-obtained enzyme retained 85% of the activity at a pH value of 6. Incidentally, a commercially available cellulase originating from *Aspergillus niger* had an activity of 0% at a pH value of 9. That is, the cellulase had no activity at a pH value of 9.

Referential Example 3

- 15 A flask was charged with 9 ml of a culture medium containing 0.5% of ammonium sulfate, 1.5% of pulp block, 0.02% of glucose, 0.1% of yeast extract, 0.02% of $MgSO_4 \cdot 7H_2O$ and 0.2% of K_2HPO_4 , and the culture medium was sterilized at 120°C for 20 minutes. The sterilized culture medium was cooled and mixed with 10 ml of 0.7% aqueous solution of $NaHCO_3$ separately sterilized. The culture medium was then inoculated with a cellulase 212-producing species belonging to the genus *Aeromonas* (deposited with the FRI deposition number of 2306), and shaking culturing was carried out at 37°C for 72 hours. Cells were removed by centrifugal separation to obtain a crude enzyme liquid of cellulase 212. The crude enzyme liquid was dried with ethanol according to the customary procedure to obtain a cellulase powder having an enzymatic activity of 0.55 unit/mg of the solid at a pH value of 6 (hereinafter referred to as "cellulase 212"). At a pH value of 9, the so-obtained enzyme retained 70% of the enzymatic activity at a pH value of 6.
- 25 Enzymes used in Examples 2 to 7 are listed as follows.
- (1) Cellulase N4
 - (2) Cellulase 212
 - (3) Cellulase (supplied by Sigma Co., originating from *Aspergillus niger*, 1.35 units/mg)
 - (4) Lipase (supplied by Gist Brochades NV, originating from *R. oryzae*)
 - (5) Amylase (Termamil 60G supplied by Novo Industries Co.)
 - (6) Protease (Alkalase 2.0M supplied by Novo Industries Co.)

Example 2

- 35 A highly alkaline powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 11.2.
- | | | | |
|----|--|-------------------|----|
| | Sodium linear-dodecylbenzene-sulfonate | 20% by weight | |
| | Soap (sodium salt of beef tallow fatty acid) | 2% by weight | |
| 40 | Sodium orthophosphate | 20% by weight | |
| | Sodium metaphosphate | 10% by weight | 40 |
| | Sodium carbonate | 15% by weight | |
| | Carboxymethyl cellulose | 1% by weight | |
| | Polyethylene glycol | 1% by weight | |
| | Fluorescent dye | 0.4% by weight | |
| 45 | Glauber salt | balance | 45 |
| | Enzyme | 0 or 2% by weight | |
| | Water | 5% by weight | |

- The results of the washing test made on so-prepared detergents are shown in Table 2. Incidentally, in Table 2 and Tables given hereinafter, each detergent is identified by example number-enzyme number (the enzyme-free detergent is identified by example number—(0)).

Table 2

	Detergent	Washing Power Index	
55	1—(0) (reference detergent)	100	
	1—(1) (present invention)	103.5	55
	1—(2) (present invention)	104.0	
	1—(3)	101	
	1—(4)	100	
	1—(5)	100	
60	1—(6)	100.5	60

Example 3

A weakly alkaline powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 10.3.

5	Sodium α -olefin-sulfonate	20% by weight	5
	Soap	1% by weight	
10	Sodium tripolyphosphate	20% by weight	10
	Sodium silicate (JIS No. 2)	10% by weight	
	Sodium carbonate	5% by weight	
	Carboxymethyl cellulose	1% by weight	
	Polyethylene glycol	1% by weight	
	Fluorescent dye	0.4% by weight	
	Glauber salt	balance	
	Enzyme	0 or 2% by weight	
	Water	10% by weight	

15 In the same manner as described in Example 1, the washing test was carried out. The obtained results are shown in Table 3. 15

Table 3

		<i>Washing Power Index</i>	
<i>Detergent</i>			
20	2—(0) (reference detergent)	100	20
	2—(1) (present invention)	104	
	2—(2) (present invention)	104.5	
	2—(4)	100	
	2—(5)	100	
25	2—(6)	100.5	25

Example 4

A neutral powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 6.8

30	Sodium linear-alcohol (C=14) sulfate	30% by weight	30
	Polyethylene glycol	1% by weight	
	Sodium phosphate	1% by weight	
	Fluorescent dye	0.2% by weight	
	Glauber salt	balance	
35	Enzyme	0 or 2% by weight	35
	Water	5% by weight	

The results of the washing test made on so-prepared detergents are shown in Table 4.

Table 4

		<i>Washing Power Index</i>	
<i>Detergent</i>			
40	3—(0) (reference detergent)	100	40
	3—(1) (present invention)	103	
	3—(2) (present invention)	103.5	
	3—(4)	100	
	3—(5)	100	
45	3—(6)	100	45

Example 5

A phosphorous-free, weakly alkaline detergent was prepared according to the following recipe.

50	Sodium linear-dodecylbenzene-sulfonate	15% by weight	50
	Sodium alkylethoxy-sulfate (C ₁₄ —C ₁₅ , EO—3 moles)	5% by weight	
	Builder and enzyme (see Table 5)	20% by weight	
55	Sodium silicate	15% by weight	55
	Sodium carbonate	15% by weight	

	Carboxymethyl cellulose	1.5% by weight	
	Polyethylene glycol	1.5% by weight	
	Fluorescent dye	0.5% by weight	
	Glauber salt	balance	
5	Water	5% by weight	5

The results of the washing test are shown in Table 5.

Table 5			
	Builder	Enzyme	Washing Power Index
10	sodium tripolyphosphate, 20%	—	100 (reference detergent)
	sodium citrate, 20%	—	98
	zeolite type 4A, 20%	—	98.5
	sodium citrate, 15%	(6), 5%	98.5
	zeolite type 4A, 15%	(6), 5%	98.5
	sodium citrate, 15%	(1), 5%	102 (present invention)
15	sodium citrate, 15%	(2), 5%	102.5 (present invention)
	zeolite type 4A, 15%	(1), 5%	101.5 (present invention)
	zeolite type 4A, 15%	(2), 5%	102 (present invention)

Example 6

Detergents were prepared according to the recipe adopted in Example 3 by using combinations of enzymes. The results of the washing test made on these detergents are shown in Table 6.

Table 6			
	Detergent	Combination of Enzymes (Right Number Indicates % of Enzyme)	Washing Power Index
25	2—(2) (reference detergent)	(2)=2	100
	2—(2)/(4) (present invention)	(2)/(4)=1/1	100.5
	2—(2)/(5) (present invention)	(2)/(5)=1/1	100.5
	2—(2)/(6) (present invention)	(2)/(6)=1/1	101
	2—(2)/(4)/(6) (present invention)	(2)/(4)/(6)=2/1/1	101.5
30	2—(2)/(5)/(6) (present invention)	(2)/(5)/(6)=2/1/1	101.5
	2—(4)/(5)/(6)	(4)/(5)/(6)=2/1/1	98

Example 7

A weakly alkaline powdery detergent for clothing was prepared according to the following recipe.

35	Sodium alkyl-sulfate ($\bar{C}=14.5$)	15% by weight	
	Sodium alkylethoxy-sulfate ($\bar{C}=14.5$, $EO=3$)	5% by weight	35
	Soap (beef tallow type)	2% by weight	
	Sodium pyrophosphate	18% by weight	
40	Sodium silicate	13% by weight	
	Sodium carbonate	5% by weight	40
	Polyethylene glycol	2% by weight	
	Fluorescent dye	0.2% by weight	
	Glauber salt	balance	
45	Magnesium silicate	1% by weight	
	Water	5% by weight	45
	Enzyme	2% by weight	
	Sodium percarbonate	15% by weight	

The results of the washing test made on so-prepared detergents are shown in Table 7.

Table 7			
	Detergent	Enzyme	Washing Power Index
50	6—(6) (reference detergent)	(6)	100
	6—(1) (present invention)	(1)	102.5
	6—(2) (present invention)	(2)	103

Claims

1. A detergent composition which includes an alkali cellulase.
2. A detergent composition as claimed in Claim 1, in which said alkali cellulase has an optimum effectiveness at a pH of 8.0 to 11.5.
- 5 3. A detergent composition as claimed in Claim 1, in which said alkali cellulase is produced by a Bacillus N fungus or a cellulase 212-producing fungus belonging to the genus Aeromonas. 5
4. A detergent composition as claimed in Claim 1, which contains 0.01 to 70 wt.% of said alkali cellulase having an enzymatic activity of at least 0.001 unit/mg solid.
5. A detergent composition as claimed in Claim 1, which contains said alkali cellulase in an amount of 0.1 to 1000 units per liter of the composition. 10
6. A detergent composition as claimed in Claim 1, which further comprises one or more of the following surfactants, divalent metal ion sequestering agents, alkali agents, inorganic electrolytes, antiredeposition agents, bleaching agents, enzymes, bluing agents, fluorescent dyes, caking-preventing agents, masking agents for factors which inhibit the alkali cellulase activity, activators for the alkali cellulase, antioxidants, solubilizers and other conventional additives. 15
7. A detergent composition as claimed in Claim 1, in which said alkali cellulase is extracted from the hepatopancreas of a marine mollusc.

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